

What is claimed is:

1. An electrolyte for dye-sensitized solar cells, wherein an oxidation-reduction substance is carried by a vulcanized rubber.

5 2. An electrolyte for dye-sensitized solar cells as claimed in claim 1, wherein the vulcanized rubber is manufactured using sulfur and/or an organic sulfur compound as a vulcanizing agent.

3. An electrolyte for dye-sensitized solar cells as claimed in claim 1 or 2, wherein the vulcanized rubber has, as side chains, an aromatic ring.

10 4. An electrolyte for dye-sensitized solar cells as claimed in claim 3, wherein the aromatic ring is a benzene ring and/or a pyridine ring.

5. An electrolyte for dye-sensitized solar cells as claimed in any one of claims 1 through 4, wherein the vulcanized rubber is impregnated
15 with a solution of the oxidation-reduction substance and is dried, thereby carrying the oxidation-reduction substance.

6. An electrolyte for dye-sensitized solar cells as claimed in any one of claims 1 through 5, wherein the carried amount of the oxidation-reduction substance is from 5 to 50% by weight relative to the
20 vulcanized rubber.

7. An electrolyte for dye-sensitized solar cells, wherein an oxidation-reduction substance is carried by a porous body comprising a high molecular material which has a three-dimensional continuous network skeleton structure.

25 8. An electrolyte for dye-sensitized solar cells as claimed in claim 7, wherein the porous body is made by mixing a high molecular material and a low molecular material in an amount much more than the high molecular material to obtain a precursor in which the high

molecular material forms a three-dimensional continuous network skeleton structure, and removing the low molecular material from the precursor.

5 9. An electrolyte for dye-sensitized solar cells as claimed in claim 7 or 8, wherein the high molecular material is an ethylene-propylene copolymer mainly consisting of ethylene and propylene, wherein the content of ethylene is 60% by weight or more.

10 10. An electrolyte for dye-sensitized solar cells as claimed in claim 8 or 9, wherein the percentage of the high molecular material in the mixture consisting of the high molecular material and the low molecular material is 30% by weight or less.

15 11. An electrolyte for dye-sensitized solar cells as claimed in any one of claims 7 through 10, wherein the average diameter of the skeleton of the three-dimensional continuous network skeleton structure of the porous body is 8 μm or less, and the average diameter of the opening of the network is 80 μm or less.

20 12. An electrolyte for dye-sensitized solar cells as claimed in any one of claims 7 through 11, wherein the porous body is impregnated with a solution of the oxidation-reduction substance and is dried, thereby carrying the oxidation-reduction substance.

13. An electrolyte for dye-sensitized solar cells as claimed in any one of claims 7 through 12, wherein the carried amount of the oxidation-reduction substance is from 5 to 90% by weight relative to the porous body.

25 14. An electrolyte for dye-sensitized solar cells, wherein an oxidation-reduction substance is carried by a phosphazene polymer.

15. An electrolyte for dye-sensitized solar cells as claimed in claim 14, wherein the phosphazene polymer is prepared by polymerizing

chain phosphazene derivatives expressed by a general formula (1):
(R¹)₃P = N-X (in the general formula (1), R¹ represents a monovalent
substituent group or a halogen element. "X" represents an organic group
containing at least one kind of element selected from a group consisting
5 of carbon, silicon, germanium, tin, nitrogen, phosphorus, oxygen, and
sulfur.).

16. An electrolyte for dye-sensitized solar cells as claimed in
claim 14, wherein the phosphazene polymer is prepared by polymerizing
cyclic phosphazene derivatives expressed by a following general
10 formula (2): (PNR²)_n (in the general formula (2), R² represents a
monovalent substituent group or a halogen element. "n" represents a
number from 2 to 14.).

17. An electrolyte for dye-sensitized solar cells as claimed in any
one of claims 14 through 16, wherein the phosphazene polymer obtained
15 has 100,000 or more molecules.

18. An electrolyte for dye-sensitized solar cells as claimed in any
one of claims 14 through 17, wherein the phosphazene polymer is
impregnated with a solution of the oxidation-reduction substance and is
dried, thereby carrying the oxidation-reduction substance.

20 19. An electrolyte for dye-sensitized solar cells as claimed in any
one of claims 14 through 18, wherein the carried amount of the
oxidation-reduction substance is from 5 to 90% by weight relative to the
phosphazene polymer.

20. An electrolyte for dye-sensitized solar cells, wherein the
25 electrolyte comprises an ethylene vinyl acetate copolymer resin film
carrying an oxidation-reduction substance.

21. An electrolyte for dye-sensitized solar cells as claimed in
claim 20, wherein the ethylene vinyl acetate copolymer resin film

contains a cross-linking agent.

22. An electrolyte for dye-sensitized solar cells as claimed in claim 20 or 21, wherein the content of vinyl acetate in the ethylene vinyl acetate copolymer resin is from 5% to 50% by weight.

5 23. An electrolyte for dye-sensitized solar cells as claimed in any one of claims 20 through 22, wherein the electrolyte is made by forming the ethylene vinyl acetate copolymer resin containing the oxidation-reduction substance into a film.

10 24. An electrolyte for dye-sensitized solar cells as claimed in any one of claims 20 through 22, wherein the ethylene vinyl acetate copolymer resin film is impregnated with a solution of the oxidation-reduction substance and is dried, thereby carrying the oxidation-reduction substance.

15 25. An electrolyte for dye-sensitized solar cells as claimed in any one of claims 20 through 24, wherein the carried amount of the oxidation-reduction substance is from 5 to 50% by weight relative to the ethylene vinyl acetate copolymer resin.

20 26. A dye-sensitized solar cell comprising a dye-sensitized semiconductor electrode, a counter electrode arranged at an opposed position to the dye-sensitized semiconductor electrode, and a solid electrolyte arranged between the dye-sensitized semiconductor electrode and the counter electrode, wherein the solid electrolyte is an electrolyte for dye-sensitized solar cells as claimed in any one of claims 1 through 25.

25 27. A method of manufacturing an electrode for dye-sensitized solar cells including a step of forming a titanium oxide thin membrane on a substrate, wherein

the titanium oxide thin membrane is formed by reactive

sputtering using a Ti metal target.

28. A method of manufacturing an electrode for dye-sensitized solar cells as claimed in claim 27, wherein TiO_x ($x < 2$) thin membrane is formed by reactive sputtering in atmosphere with controlled oxygen
5 concentration.

29. A method of manufacturing an electrode for dye-sensitized solar cells as claimed in claim 28, wherein the oxygen concentration is controlled by plasma emission control.

30. A method of manufacturing an electrode for dye-sensitized
10 solar cells as claimed in claim 28, wherein the oxygen concentration is controlled by plasma impedance control.

31. A method of manufacturing an electrode for dye-sensitized solar cells as claimed in any one of claims 27 through 30, wherein the reactive sputtering is conducted by using a dual cathode system and by
15 alternately applying voltage to two cathodes arranged in parallel.

32. A method of manufacturing an electrode for dye-sensitized solar cells as claimed in any one of claims 27 through 31, wherein the substrate is an organic resin film.

33. An electrode for dye-sensitized solar cells manufactured by a
20 method as claimed in any one of claims 27 through 32.

34. An electrode for dye-sensitized solar cells comprising a titanium oxide thin membrane on an organic resin film, wherein the titanium oxide thin membrane is formed by a reactive sputtering using a Ti metal target.

25 35. An electrode for dye-sensitized solar cells as claimed in claim 33 or 34, wherein the titanium oxide thin membrane is a TiO_x ($x < 2$) thin membrane.

36. An organic dye-sensitized solar cell comprising a transparent

substrate having a transparent electrode on a surface thereof, an organic dye-sensitized metal oxide semiconductor electrode having a metal oxide semiconductor membrane formed on the transparent electrode and organic dye adsorbed in a surface of the semiconductor membrane, a
5 counter electrode arranged at an opposed position to the electrode, and a redox electrolyte filled between these electrodes, wherein

an antireflective membrane is formed on a surface of said transparent substrate at a side where no transparent electrode is formed.

37. An organic dye-sensitized solar cell comprising a transparent
10 substrate having a transparent electrode on a surface thereof, an organic dye-sensitized metal oxide semiconductor electrode having a metal oxide semiconductor membrane formed on the transparent electrode and organic dye adsorbed in a surface of the semiconductor membrane, a counter electrode arranged at an opposed position to the electrode, and a
15 redox electrolyte filled between these electrodes, wherein

an antireflective film having an antireflective membrane is attached to a surface of said transparent substrate at a side where no transparent electrode is formed via an adhesive layer.

38. An organic dye-sensitized solar cell as claimed in claim 36 or
20 37, wherein the antireflective membrane reduces the reflectance in a wavelength in which the absorbancy of the organic dye is maximum.

39. An organic dye-sensitized solar cell as claimed in claim 36 or 37, wherein the antireflective membrane has minimum reflectance in a wavelength in which the absorbancy of the organic dye is maximum.

25 40. An organic dye-sensitized solar cell as claimed in any one of claims 37 through 39, wherein the antireflective membrane comprises a transparent polymer film and an antireflective membrane formed on the transparent polymer film.

41. An organic dye-sensitized solar cell as claimed in any one of claims 36 through 40, wherein said antireflective film is an inorganic laminated membrane consisting of, in top-to-bottom order, low-refractive transparent inorganic thin membrane(s) and
5 high-refractive transparent inorganic thin membrane(s) which are alternately laminated.

42. An organic dye-sensitized solar cell as claimed in claim 41, wherein a low-refractive transparent organic thin membrane is provided instead of the upper-most low-refractive transparent inorganic thin
10 membrane.

43. An organic dye-sensitized solar cell as claimed in any one of claims 37 through 42, wherein said antireflective film has an ultraviolet protection layer between the transparent polymer film and the antireflective membrane formed on the transparent polymer film.

15 44. An organic dye-sensitized solar cell as claimed in any one of claims 41 through 43, wherein said high-refractive transparent inorganic thin membrane is a thin membrane having refractive index of 1.8 or more made of ITO (indium tin oxide), ZnO, Al-doped ZnO, Al-doped TiO₂, Al-doped SnO₂, or ZrO.

20 45. An organic dye-sensitized solar cell as claimed in any one of claims 41 through 44, wherein said low-refractive transparent inorganic thin membrane is a thin membrane having refractive index of 1.6 or less made of SiO₂, MgF₂, or Al₂O₃.

25 46. An organic dye-sensitized solar cell as claimed in any one of claims 37 through 45, wherein said adhesive layer contains ethylene-vinyl acetate copolymer or sticky acrylic resin.

47. An organic dye-sensitized solar cell as claimed in any one of claims 37 through 46, wherein the metal oxide semiconductor membrane

is formed by the vapor deposition.

48. An organic dye-sensitized solar cell as claimed in claim 47, wherein the vapor deposition is physical deposition, vacuum deposition, sputtering, ion plating, CVD, or plasma CVD.

5 49. An organic dye-sensitized solar cell as claimed in claim 48, wherein the vapor deposition is a facing targets sputtering method or a dual cathode type sputtering method.

50. An organic dye-sensitized solar cell as claimed in claim 48 or 49, wherein the vapor deposition is a reactive sputtering method.

10 51. An organic dye-sensitized solar cell as claimed in any one of claims 36 through 50, wherein the metal oxide semiconductor membrane is made of titanium oxide, zinc oxide, tin oxide, antimony oxide, niobium oxide, tungsten oxide, indium oxide, or any of these metal oxides doped with other metal or other metal oxide.

15 52. An organic dye-sensitized solar cell as claimed in any one of claims 36 through 51, wherein the metal oxide semiconductor membrane is made of titanium oxide.

53. An organic dye-sensitized solar cell as claimed in claim 52, wherein the metal oxide semiconductor membrane is made of
20 anatase-type titanium dioxide.

54. An organic dye-sensitized solar cell as claimed in any one of claims 36 through 53, wherein the thickness of the metal oxide semiconductor membrane is 10 nm or more.

25 55. An organic dye-sensitized solar cell as claimed in any one of claims 36 through 54, wherein the organic dye is a ruthenium containing dye (ruthenium phenanthroline, ruthenium diketonate) and the antireflective membrane has a light reflectance of 10% or less in a range of wavelength from 300 to 600 nm.

56. An organic dye-sensitized solar cell as claimed in any one of claims 36 through 54, wherein the organic dye is a coumarin derivative dye and the antireflective membrane has a light reflectance of 10% or less in a range of wavelength from 400 to 600 nm.

5 57. An organic dye-sensitized solar cell comprising a transparent substrate having a transparent electrode on a surface thereof, an organic dye-sensitized metal oxide semiconductor electrode having a metal oxide semiconductor membrane formed on the transparent electrode and organic dye adsorbed in a surface of the semiconductor membrane, a
10 counter electrode arranged at an opposed position to the electrode, and a redox electrolyte filled between these electrodes, wherein

the transparent substrate is a transparent organic polymer substrate and the counter electrode is formed on an organic polymer substrate.

15 58. An organic dye-sensitized solar cell as claimed in claim 57, wherein a transparent electrode is provided between the counter electrode and the organic polymer substrate.

59. An organic dye-sensitized solar cell as claimed in claim 57 or 58, wherein the organic polymer substrate having the counter electrode
20 has a high reflectance.

60. An organic dye-sensitized solar cell as claimed in any one of claims 57 through 59, wherein the organic polymer substrate having the counter electrode has a pattern or is colored.

61. An organic dye-sensitized solar cell as claimed in any one of
25 claims 57 through 60, wherein the organic polymer substrate having the counter electrode is a transparent substrate.

62. An organic dye-sensitized solar cell as claimed in any one of claims 57 through 61, wherein the material of the transparent organic

polymer substrate or the organic polymer substrate is polyethylene terephthalate, polycarbonate, polymethyl methacrylate, or fluorocarbon resin.

5 63. An organic dye-sensitized solar cell as claimed in any one of claims 57 through 62, wherein the metal oxide semiconductor membrane is formed by vapor deposition.

64. An organic dye-sensitized solar cell as claimed in claim 63, wherein the vapor deposition is physical deposition, vacuum deposition, sputtering, ion plating, CVD, or plasma CVD.

10 65. An organic dye-sensitized solar cell as claimed in claim 64, wherein the vapor deposition is a facing targets sputtering method, a dual cathode type sputtering method, or a reactive sputtering method.

66. An organic dye-sensitized solar cell as claimed in any one of claims 57 through 65, wherein the metal oxide semiconductor membrane
15 is made of titanium oxide, zinc oxide, tin oxide, antimony oxide, niobium oxide, tungsten oxide, indium oxide, or any of these metal oxides doped with other metal or other metal oxide.

67. An organic dye-sensitized solar cell as claimed in claim 66, wherein the metal oxide semiconductor membrane is made of titanium
20 oxide.

68. An organic dye-sensitized solar cell as claimed in claim 67, wherein the metal oxide semiconductor membrane is made of anatase-type titanium dioxide.

69. An organic dye-sensitized solar cell as claimed in any one of
25 claims 57 through 68, wherein a release film is attached to the back surface of the organic polymer substrate having the counter electrode via an adhesive layer.

70. An organic dye-sensitized solar cell as claimed in claim 69,

wherein the adhesive layer contains ethylene-vinyl acetate copolymer or sticky acrylic resin.

71. A building material having an organic dye-sensitized solar cell as claimed in any one of claims 57 through 70, wherein the back
5 surface of the transparent organic polymer substrate having the counter electrode is bonded to a surface of a base material via an adhesive layer.

72. A building material as claimed in claim 71, wherein the base material is a window pane.

73. A building material as claimed in claim 71, wherein the base
10 material is a roofing material.

74. A method of forming a metal oxide semiconductor membrane having a large surface area, wherein coating liquid in which metal oxide microparticles are dispersed in a binder is applied to a substrate having a transparent electrode formed on a surface thereof and is dried so as to
15 form a metal oxide containing coating, and the metal oxide containing coating is subjected to ultraviolet irradiation treatment so as to remove the binder, thereby forming a metal oxide semiconductor membrane having a large surface area.

75. A method as claimed in claim 74, wherein the wavelength of
20 ultraviolet light to be used for the ultraviolet irradiation treatment is in a range of from 1 to 400 nm.

76. A method as claimed in claim 74 or 75, wherein the ultraviolet irradiation treatment is conducted in the presence of gas of at least one selected from a group consisting of ozone, oxygen, fluorine
25 atom containing compound, and chlorine atom containing compound gases.

77. A method as claimed in any one of claims 74 through 76, wherein the metal oxide semiconductor membrane is a membrane which

is made of substantially only a metal oxide.

78. A method as claimed in any one of claims 74 through 77,
wherein the metal oxide is titanium oxide, zinc oxide, tin oxide,
antimony oxide, niobium oxide, tungsten oxide, indium oxide, or any of
5 these metal oxides doped with other metal or other metal oxide.

79. A method as claimed in claim 78, wherein the metal oxide is
titanium oxide.

80. A method as claimed in claim 79, wherein the metal oxide is
anatase-type titanium dioxide.

10 81. A method as claimed in any one of claims 74 through 80,
wherein the primary diameter of the metal oxide microparticles is in a
range of from 0.001 to 5 μm .

82. A method as claimed in any one of claim 74 through 81,
wherein the metal oxide semiconductor membrane is made of titanium
15 oxide, zinc oxide, tin oxide, antimony oxide, niobium oxide, tungsten
oxide, indium oxide, or any of these metal oxides doped with other
metal or other metal oxide.

83. A method as claimed in claim 82, wherein the metal oxide
semiconductor membrane is titanium oxide.

20 84. A method as claimed in claim 83, wherein the metal oxide
semiconductor membrane is anatase-type titanium dioxide.

85. A method as claimed in any one of claims 74 through 84,
wherein the binder is an organic polymer.

86. a method s claimed in any one of claims 74 through 85,
25 wherein the thickness of the metal oxide semiconductor membrane is 10
nm or more.

87. An organic dye-sensitized metal oxide semiconductor
electrode including a substrate having a transparent electrode on the

surface thereof and a metal oxide semiconductor membrane formed on the transparent electrode which are obtained by a method as claimed in any one of claims 74 through 86, and an organic dye adsorbed in the surface of the semiconductor membrane.

5 88. An organic dye-sensitized solar cell comprising an organic dye-sensitized metal oxide semiconductor electrode as claimed in claim 87, a counter electrode arranged at an opposed position to the organic dye-sensitized metal oxide semiconductor electrode, and a redox electrolyte filled between these electrodes.

10 89. A method of forming a transparent electrode, wherein coating liquid in which conductive metal oxide microparticles are dispersed in a binder is applied to a surface of a substrate and is dried so as to form a conductive metal oxide containing coating, the binder is then removed from the conductive metal oxide containing coating so as to form a
15 coating-type transparent electrode membrane, and a conductive metal oxide is deposited on the coating-type transparent electrode membrane by vapor deposition so as to form a vapor deposition-type transparent electrode membrane, thereby providing a lamination-type transparent electrode.

20 90. A method of forming a transparent electrode, wherein a conductive metal oxide is deposited on a surface of a substrate so as to form a vapor deposition-type transparent electrode membrane by vapor deposition, coating liquid in which conductive metal oxide
25 microparticles are dispersed in a binder is applied to the vapor deposition-type transparent electrode membrane and is dried so as to form a conductive metal oxide containing coating, and then the binder is removed from the conductive metal oxide containing coating so as to form a coating-type transparent electrode membrane, thereby providing

a lamination-type transparent electrode.

91. A method as claimed in claim 89 or 90, wherein the binder is removed by plasma treatment.

92. A method as claimed in claim 91, wherein the plasma
5 treatment is conducted with high-frequency plasma, microwave plasma, or a hybrid type thereof.

93. A method as claimed in claim 91 or 92, wherein the plasma treatment is conducted in the presence of gas of at least one selected from a group consisting of oxygen, fluorine, and chlorine gases.

10 94. A method as claimed in claim 89 or 90, wherein the binder is removed by ultraviolet irradiation treatment.

95. A method as claimed in claim 94, wherein the wavelength of ultraviolet light to be used for the ultraviolet irradiation treatment is in a range of from 1 to 400 nm.

15 96. A method as claimed in claim 94 or 95, wherein the ultraviolet irradiation treatment is conducted in the presence of gas of at least one selected from a group consisting of ozone, oxygen, fluorine atom containing compound and chlorine atom containing compound gases.

20 97. A method as claimed in any one of claims 89 through 96, wherein the conductive metal oxide is at least one of selected from a group consisting of In_2O_3 : Sn(ITO), SnO_2 :Sb, SnO_2 :F, ZnO :Al, SnO_2 , ZnO :F, and CdSnO_4 .

25 98. A method as claimed in any one of claims 89 through 97, wherein the coating-type transparent electrode membrane is a membrane which is made of substantially only a conductive metal oxide.

99. A method as claimed in any one of claims 89 through 98, wherein the primary particle diameter of the conductive metal oxide

microparticles is in a range of from 0.001 to 5 μm .

100. A method as claimed in any one of claims 89 through 99, wherein the binder is polyalkylene glycol.

101. A method as claimed in any one of claims 89 through 100,
5 wherein the vapor deposition for forming the vapor deposition-type transparent electrode membrane is physical deposition, vacuum deposition, sputtering, ion plating, CVD, or plasma CVD.

102. A method as claimed in any one of claims 89 through 101,
10 wherein the vapor deposition-type transparent electrode membrane is at least one of selected from a group consisting of In_2O_3 : Sn(ITO), SnO_2 :Sb, SnO_2 :F, ZnO :Al, SnO_2 , ZnO :F, and CdSnO_4 .

103. A method as claimed in any one of claims 89 through 102, wherein the thickness of the vapor deposition-type transparent electrode membrane is in a range of from 0.1 to 100 nm.

15 104. A method as claimed in any one of claims 89 through 103, wherein the thickness of the coating-type transparent electrode membrane is in a range of from 10 to 500 nm.

105. A transparent electrode substrate having a transparent electrode membrane which is formed on a substrate surface according to
20 a method as claimed in any one of claims 89 through 104.

106. A method of forming a metal oxide semiconductor membrane including a step of forming a metal oxide semiconductor membrane on a transparent electrode of a transparent electrode substrate as claimed in claim 105 by vapor deposition.

25 107. A method as claimed in claim 106, wherein the vapor deposition is physical deposition, vacuum deposition, sputtering, ion plating, CVD, or plasma CVD.

108. A method as claimed in claim 106, wherein the metal oxide

semiconductor membrane is a membrane formed by depositing titanium oxide, zinc oxide, tin oxide, antimony oxide, niobium oxide, tungsten oxide, indium oxide, or any of these metal oxides doped with other metal or other metal oxide by vapor deposition.

5 109. A method as claimed in claim 108, wherein the metal oxide semiconductor membrane is made of titanium oxide.

 110. A method as claimed in claim 109, wherein the metal oxide semiconductor membrane is made of anatase-type titanium dioxide.

10 111. An organic dye-sensitized metal oxide semiconductor electrode including a substrate having a transparent electrode on the surface thereof and a metal oxide semiconductor membrane formed on the transparent electrode which are obtained by a method as claimed in any one of claims 106 through 110, and an organic dye adsorbed in the surface of the semiconductor membrane.

15 112. An organic dye-sensitized solar cell comprising an organic dye-sensitized metal oxide semiconductor electrode as claimed in claim 111, a counter electrode arranged at an opposed position to the organic dye-sensitized metal oxide semiconductor electrode, and a redox electrolyte filled between these electrodes.

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